

AD-A054 668

CALIFORNIA UNIV LOS ANGELES DEPT OF CHEMISTRY

F/G 20/12

THE TWO-PHOTON EXCITATION SPECTRUM OF TRIPHENYLENE IN N-HEPTANE--ETC(U)

APR 78 A MERLE, A CAMPION, M A EL-SAYED

N00014-75-C-0602

UNCLASSIFIED

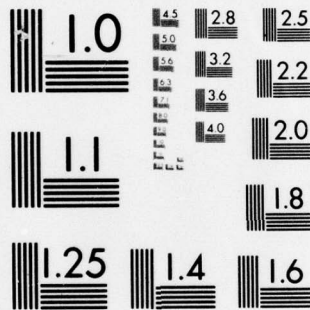
TR-29

NL

| OF |  
AD  
A054668



END  
DATE  
FILMED  
6 -78  
DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

FOR FURTHER TRAN

12  
act

AD A 054668

AD No.   
DDC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract No. <sup>15</sup> N00014-75-C-0602

Task No. NR-056-498

9 Interim TECHNICAL REPORT, p. 29

6 THE TWO-PHOTON EXCITATION SPECTRUM OF TRIPHENYLENE  
IN n-HEPTANE SINGLE CRYSTALS.

14 TR-29

by

10 Anne-Marie Merle, Alan Campion M. A. El-Sayed  
Department of Chemistry  
University of California  
Los Angeles, California 90024

Prepared for Publication

in

Chemical Physics Letters

DDC  
RECEIVED  
JUN 6 1978  
E

Reproduction in whole or in part is permitted for any  
purpose of the United States Government

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

11 19 Apr 1978

12 15p.

072 255

Shu

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE   |                       | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM                                  |
|---|-----------------------|--|
| 1. REPORT NUMBER<br>Technical Report No. 29 ✓   | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER  |
| 4. TITLE (and Subtitle)<br>THE TWO-PHOTON EXCITATION SPECTRUM OF TRIPHENYLENE<br>IN n-HEPTANE SINGLE CRYSTALS   |                       | 5. TYPE OF REPORT & PERIOD COVERED<br>Interim Technical Report ✓             |
|   |                       | 6. PERFORMING ORG. REPORT NUMBER   |
| 7. AUTHOR(s)<br>Anne-Marie Merle, Alan Campion and M. A. El-Sayed   |                       | 8. CONTRACT OR GRANT NUMBER(s)<br>N00014-75-C-0602 ✓                         |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Regents of the University of California<br>University of California, 405 Hilgard Ave.<br>Los Angeles, California 90024   |                       | 10. PROGRAM ELEMENT, PROJECT, TASK<br>AREA & WORK UNIT NUMBERS<br>NR-056-498 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>Office of Naval Research<br>Chemistry Branch<br>Arlington, Virginia 22217  |                       | 12. REPORT DATE<br>April 19, 1978 ✓  |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)<br>Office of Naval Research<br>Branch Office<br>1030 East Green Street<br>Pasadena, California 91106  |                       | 13. NUMBER OF PAGES<br>13  |
| 16. DISTRIBUTION STATEMENT (of this Report)<br><br>Distribution of this document is unlimited.  |                       | 15. SECURITY CLASS. (of this report)<br><br>UNCLASSIFIED                     |
|   |                       | 15a. DECLASSIFICATION/DOWNGRADING<br>SCHEDULE                                |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  |                       |  |
| 18. SUPPLEMENTARY NOTES<br><br>To be published in Chemical Physics Letters  |                       |  |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br><br>Two-photon processes<br>Triphenylene<br>Excited states<br>Assignments of electronic states  |                       |  |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>A comparison of the one- and two-photon absorption spectra of triphenylene in n-heptane single crystals at 1.6 K reveals that the lowest singlet state ( $S_1$ ) is of $D_{2h}$ symmetry while the second singlet state ( $S_2$ ) has $D_{2h}$ symmetry, in contradiction with the commonly accepted assignment. |                       |  |

The Two-Photon Excitation Spectrum of Triphenylene  
in n-Heptane Single Crystals

Anne-Marie Merle\*, Alan Campion\*\*, and M. A. El-Sayed

Department of Chemistry†  
University of California  
Los Angeles California 90024

Abstract

A comparison of the one- and two-photon absorption spectra of triphenylene in n-heptane single crystals at 1.6 K reveals that the lowest singlet state ( $S_1$ ) is of  $^1A_1$  symmetry while the second singlet state ( $S_2$ ) has  $^1A_2$  symmetry, in contradiction with the commonly accepted assignment.

---

\* Present address: Laboratoire de Chimie Physique A  
Universite de Bordeaux  
351 Cours de la Liberation  
33405 Talence, FRANCE

\*\*Present address: Department of Chemistry, University of California  
Berkeley CA 94720

† Contribution No. 3989

|   |                       |
|---|-----------------------|
| Section <input checked="" type="checkbox"/> |                       |
| action <input type="checkbox"/>             |                       |
| <input type="checkbox"/>                    |                       |
| JUSTIFICATION.....                          |                       |
| BY.....                                     |                       |
| DISTRIBUTION/AVAILABILITY CODES             |                       |
| Dist.                                       | AVAIL. and/or SPECIAL |
| A   |                       |



## I. Introduction

The lowest two excited singlet electronic states of triphenylene are observed at  $29200\text{ cm}^{-1}$  and  $33200\text{ cm}^{-1}$  and have been assigned as the  ${}^1L_b$  and  ${}^1L_a$  states respectively.<sup>(1)</sup> Calculation predicts these states to lie  $30000\text{ cm}^{-1}$  ( ${}^1L_b$ ) and  $33500\text{ cm}^{-1}$  ( ${}^1L_a$ ) above the ground state.<sup>(2,3)</sup> Their transitions to the ground state are electric dipole forbidden. The commonly accepted assignments<sup>(4-6)</sup> for the symmetry of these states is based upon the correlation between the  $D_{6h}$  (benzene) and  $D_{3h}$  (triphenylene) point groups leading to an  $A'_2$  symmetry for  $S_1$  and an  $A'_1$  symmetry for  $S_2$ . Unfortunately, however, this assignment was made assuming that the  $C'_2$  axis (which passes through the carbon atoms) is preserved upon symmetry reduction. Since the  $C''_2$  axis (which bisects the C-C bonds) is in fact the symmetry axis that is retained, the correct correlation predicts that the lowest excited singlet state  $S_1$  should have  $A'_1$  symmetry and  $S_2$  should have  $A'_2$  symmetry. Unfortunately, the one-photon selection rules predict the transitions from the ground state to either the  ${}^1A'_1$  or  ${}^1A'_2$  excited states to be symmetry forbidden. Thus the analysis of the previously observed fluorescence spectrum<sup>(5,7)</sup> cannot distinguish between a  ${}^1A'_1$  or a  ${}^1A'_2$  assignment for the lowest excited state.

One-photon spectroscopy is unable to make a definitive assignment of the first two excited singlet states of triphenylene. Two-photon spectroscopy, however, appears to be an appropriate technique for making a distinction between the two possible  ${}^1A'_1$  and  ${}^1A'_2$  assignments. The selection rules<sup>(8,9)</sup> for two-photon absorption predict that the transition from the ground state to a  ${}^1A'_1$  excited state is symmetry allowed whereas transitions to the  ${}^1A'_2$  excited state are symmetry forbidden.

The two-photon excitation spectrum of the second singlet state of triphenylene in polymethylmethacrylate at 77 K has been reported.<sup>(6)</sup> A broad structureless band centered at  $33200\text{ cm}^{-1}$  was observed and attributed to the 0,0 transition of an

allowed  $S_2 \rightarrow S_0$  transition. The authors concluded that  $S_2$  has a  $^1A'_1$  symmetry and consequently  $S_1$  has a  $^1A'_2$  symmetry. The use of a glass matrix prevented the observation of any structure in the spectrum and, in particular, of a weak 0,0 transition indicative of a forbidden two-photon  $S_2 \rightarrow S_0$  transition (as predicted by the  $D_{6h} \rightarrow D_{3h}$  correlation described above). The definitive symmetry assignment of the electronic states of triphenylene required the examination of the high resolution two-photon spectrum. In this letter we give the results on the two-photon excitation spectrum of triphenylene in an *n*-heptane single crystal (Shpol'skii's matrix) at 1.6 K. This matrix is quite appropriate for such a study as it exhibits the Shpol'skii effect so that the electronic spectra of the guest are sharp and (for triphenylene in *n*-heptane) they do not exhibit the multiplet structure often observed in Shpol'skii spectra of other systems. The use of single crystals appeared to be an experimental requirement for the observation of the two-photon spectrum as it minimizes the scattered light. It has furthermore been shown<sup>(10,11)</sup> that they allow the study of oriented isolated guest molecules so that the polarization of the two-photon spectrum can also be investigated in these crystals. The orientation of triphenylene in *n*-heptane single crystals has been previously determined by ESR<sup>(12)</sup> and the molecule has been found to lie in the substitutional plane of the lattice defined by the heptane chain axis and the crystallographic (c) axis.<sup>(11)</sup>

The two-photon excitation spectrum of triphenylene has been obtained by monitoring the phosphorescence emission, a technique which was first used on pyrazine crystals.<sup>(9)</sup> This method is suitable for triphenylene, as its quantum yield of phosphorescence is an order of magnitude higher than that for fluorescence.<sup>(13)</sup> A comparison of the observed sharp one- and two-photon spectra clearly shows that, contrary to previous work,  $S_1$  is of  $^1A'_1$  symmetry and  $S_2$  is of  $^1A'_2$  symmetry.

## II. Experimental

Triphenylene and heptane were obtained from Fluka. Single crystals were grown by slowly cooling the degassed solutions, and were cleaved along the (ab) and (ac) faces. All spectra were taken at 1.6 K.

A Molelectron DL-200 N<sub>2</sub> laser pumped dye laser was used as the excitation source and a gated photon counter<sup>(9)</sup> measured the intensity of the undispersed phosphorescence, which was detected by an EMI 6256S photomultiplier. The photomultiplier was protected from scattered laser light by a Corning 7-59 glass filter. The laser intensity was monitored by a Motorola MRD-500 photodiode whose output was fed into a PAR 162 boxcar integrator with the 163 sampling head (1 ns aperture). The laser wavelength, laser intensity and phosphorescence intensity data were processed by an on-line PDP-11/45 computer, which normalized the spectrum to an  $I^2$  dependence.

Four dye solutions covered the wavelength range 6850 to 5950 Å: Nile blue and Rhodamine B, Cresyl Violet and Rhodamine 6G, Rhodamine B, and Rhodamine 6G.

The laser light was polarized by an extra-cavity linear polarizer and the plane of polarization was then rotated by a half-wave Fresnel Rhomb to the desired angle.

## III. Results

### 1. Assignment of the first excited singlet state ( $S_1$ ) of triphenylene:

The normalized two-photon excitation spectrum of  $S_1$  is presented in Fig. 1B. An interpretation of this spectrum is made easier by comparing it with the one-photon excitation spectrum which is presented in Fig. 1A. The vibronic analysis of this latter spectrum has never been reported. The 0,0 transition is forbidden but appears very weakly at 3430.5 Å because of the reduced symmetry of triphenylene due to matrix effects. The prominent vibrations of the one-photon excitation spectrum have  $e'$  symmetry and occur at frequencies very close



to those observed in the fluorescence spectrum (Table 1).<sup>(5,7)</sup> The high intensity of the  $0,780\text{ cm}^{-1}$  band in the one-photon spectrum allows us to assign it as a false origin. This is confirmed by the fact that the  $a'_1$  vibrations --  $424\text{ cm}^{-1}$ ,  $666\text{ cm}^{-1}$ ,  $1147\text{ cm}^{-1}$ ,  $1227\text{ cm}^{-1}$  and  $1346\text{ cm}^{-1}$  -- appear in the one-photon spectrum built on the  $0,780\text{ cm}^{-1}$  false origin. The general features of the one-photon spectrum, i.e., the weak 0,0 band, and the strong  $e'$  false origin bands on which totally symmetric vibrations are built, leave little doubt that the one-photon transition to  $S_1$  is symmetry forbidden.

The most striking feature in the two-photon spectrum, on the other hand, is the strong intensity of its 0,0 band at  $6860.9\text{ \AA}$  ( $29151\text{ cm}^{-1}$ ) which appears as the most intense band in the spectrum. The analysis of the two-photon vibronic structure is summarized in Table 1. The spectrum is composed mainly of totally symmetric  $a'_1$  vibrations, which confirms that it is two-photon allowed. Note that the main  $e'$  vibrations appearing as false origins in the one-photon excitation spectrum do not appear in the two-photon spectrum. Thus the analysis of the two-photon spectrum strongly suggests that the  $S_1 \leftarrow S_0$  transition is two-photon allowed. This conclusion, combined with the fact that this transition is one-photon forbidden, leads to the assignment of  $^1A'_1$  (and not  $^1A'_2$  as was previously given)<sup>(6)</sup> for the  $S_1$  state in triphenylene.

Polarization measurements on the two-photon spectrum provide evidence that the 0,0 band and the totally symmetric vibrations are in-plane polarized since the maximum intensity ( $I_{||}$ ) was observed when the light was polarized along the direction of the intersection between the triphenylene plane and the crystallographic (ab) or (ac) faces.<sup>(11)</sup> When the light was polarized perpendicularly to this direction, the intensity ( $I_{\perp}$ ) was observed to be 10% of the value found for  $I_{||}$ . In-plane polarization of the 0,0 band suggests that the virtual intermediate state of the two-photon process is a  $\pi, \pi^* E'$  state. The other possible intermediate state is a  $\sigma, \pi^* A''_2$  state which would give rise to an out-

of-plane polarization. A  $\pi, \pi^*$  intermediate state is however more likely as transitions to these states are known to have oscillator strengths which are much higher than those for  $\sigma, \pi$  states.

## 2. Assignment of the second excited singlet state ( $S_2$ ):

The one- and two-photon excitation spectra of the  $S_2 \leftarrow S_0$  transition are presented in Figs. 2A and 2B and show much broader bands than the  $S_1$  excitation spectra. There is a strong similarity between these two spectra which suggests without further analysis that the two-photon spectrum is, as is the one-photon spectrum, electric dipole forbidden. Therefore only the vibrational analysis of the two-photon spectrum is presented in Table 2.

The interpretation of the excitation spectrum to the  $S_2$  state is made more difficult because of possible overlapping with bands that belong to the  $S_1 \leftarrow S_0$  transition. Neither the one- or two-photon spectra shows an intense band in the predicted region of the 0,0 transition but only a very weak band at  $32403 \text{ cm}^{-1}$ . The fact that the main  $e'$  vibrations of triphenylene can be found built on this band strongly suggests that it is the 0,0 transition. This assignment corresponds to a gap of  $2890 \text{ cm}^{-1}$  between the first and second singlet states and is in agreement with the value of  $2830 \text{ cm}^{-1}$  which has been calculated.<sup>(14)</sup> The weakness of this band, the great similarity between the one- and two-photon spectra, and the occurrence of non-totally symmetric vibrations allow us to conclude that the two-photon excitation spectrum is electric dipole forbidden and induced by vibronic coupling.

We can thus assign a  ${}^1A_2'$  symmetry to the second excited singlet state of triphenylene as its excitation spectrum is both one- and two-photon forbidden. This spectrum is vibronically induced by coupling with  $E'$  and  $E''$  higher excited singlet states, as the main  $e'$  and some  $e''$  vibrations that appear in the one-photon excitation spectrum of  $S_1$  can also be detected in the  $S_2$  spectrum.

#### IV. Conclusion

A comparison of the observed one- and two-photon spectra of triphenylene has allowed us to assign the symmetries of the first two excited singlet states  $S_1, S_2$  of triphenylene. The large differences between the observed one- and two-photon spectra of  $S_1$  provide strong evidence that  $S_1$  has a  $^1A_1'$  symmetry (to which one-photon transition is forbidden but two-photon absorption is allowed).

On the contrary, the similarity of the one- and two-photon spectra of  $S_2$ , which appear to result from symmetry forbidden transitions in both cases, proves that this state has a  $^1A_2'$  symmetry.

Acknowledgment: The authors wish to thank the U.S. Office of Naval Research for financial support.



## References

1. H. Klevens and J. Platt, J. Chem. Phys. 17 (1949) 470.
2. N. Ham and K. Ruedenberg, J. Chem. Phys. 25 (1956) 113.
3. H. Zimmermann and N. Joop, J. Elektrochem 65 (1961) 138.
4. R. S. Becker, I. S. Singh and E. A. Jackson, J. Chem. Phys. 38(a) (1963) 2144.
5. Z. Ruzievicz, Acta Physica Polonica 28, 3 (1965) 389.
6. L. Singer, Z. Baram, A. Rom and S. Kimel, Chem. Phys. Lett. 47, 2 (1977) 372.
7. M. Lamotte, S. Risemberg, A. M. Merle and J. Jousot Dubien, Chem. Phys. (to be published).
8. R. M. Hochstrasser and J. E. Wessel, Chem. Phys. Lett. 24, 1 (1976) 1.
9. P. Esherick, P. Zinsli and M. A. El-Sayed, Chem. Phys. 10 (1975) 415.
10. M. Lamotte, A. M. Merle, J. Jousot Dubien and F. Dupuey, Chem. Phys. Lett. 35 (1975) 410.
11. A. M. Merle, M. Lamotte, S. Risemberg, C. Hauw, J. Gaultier and J. P. Grivet, Chem. Phys. 22 (1977) 207.
12. A. M. Merle, M. Lamotte and H. Kooter, C. R. Acad. Sci. C (to be published).
13. A. A. Lamola and G. S. Hammond, J. Chem. Phys. 43 (1965) 2129.
14. J. Pancir and R. Zahradnick, J. Phys. Chem. 77 (1973) 121.
15. V. Schettino, J. Mol. Spectros. 34 (1970) 78.



Table 1. The analysis<sup>†</sup> of the one- and two-photon excitation spectra of the  $S_1 \leftarrow S_0$  transition.

| one-photon excitation of $S_1$ |                              | Possible assignment and ground state vibrations |             | two-photon excitation of $S_1$   |                              |
|--------------------------------|------------------------------|---|-------------|----------------------------------|------------------------------|
| $h\nu$ cm <sup>-1</sup>        | $\Delta\nu$ cm <sup>-1</sup> |   |             | $2 \times h\nu$ cm <sup>-1</sup> | $\Delta\nu$ cm <sup>-1</sup> |
| 29150 w                        |                              |   | 0,0         | 29151 s                          |                              |
| 29403 w                        | 253                          | e'  | 254         |                                  |                              |
| 29425 m                        | 275                          | e''   | 279         |                                  |                              |
|                                |                              | a <sub>1</sub> '                                | 418         | 29575 w                          | 424                          |
| 29775 m                        | 625                          | e'  | 619         |                                  |                              |
|                                |                              | a <sub>1</sub> '                                | 685         | 29817 m                          | 666                          |
| 29931 s                        | 781                          | e'  | 775         |                                  |                              |
|                                |                              | e''   | 936         | 30086 m                          | 935                          |
| 30202 w                        | 1052                         | e'  | 1052        | 30198 w                          | 1047                         |
|                                |                              | a <sub>1</sub> '                                | 1180        | 30298 m                          | 1147                         |
| 30340 w                        | 1190                         | e'  | 1187        |                                  |                              |
|                                |                              | a <sub>1</sub> '                                | 1230        | 30378 m                          | 1227                         |
| 30440 w                        | 1290                         | e'  | 1300        | 30442 w                          | 1291                         |
|                                |                              |   |             | 30456 m                          | 1305                         |
|                                |                              | 2 × a <sub>1</sub> '                            | (667)       | 30478 w                          | 1327                         |
|                                |                              | a <sub>1</sub> '                                | 1346        | 30497 m                          | 1346                         |
| 30506 m                        | 1356                         |   |             |                                  |                              |
|                                |                              |   |             | 30525 m                          | 1374                         |
| 30581 w                        | 1431                         | e'  | 1434        |                                  |                              |
|                                |                              | a <sub>1</sub> '                                | 1458        | 30600 w                          | 1449                         |
| 30609 m                        | 1459                         | e'  | 1497        |                                  |                              |
| 30652 w                        | 1502                         | e'  | 1505        | 30656 w                          | 1505                         |
|                                |                              | a <sub>1</sub> '                                | 1550        | 30663 m                          | 1512                         |
| 30750 w                        | 1600                         | e' + a <sub>1</sub> '                           | (253+1346)  |                                  |                              |
| 30969 w                        | 1819                         | e' + a <sub>1</sub> '                           | (780+1148)  |                                  |                              |
|                                |                              | 3 × a <sub>1</sub> '                            | (667)       | 31138 w                          | 1987                         |
| 31177 w                        | 2027                         | e' + a <sub>1</sub> '                           | (780+1227)  |                                  |                              |
| 31299 m                        | 2149                         | e' + a <sub>1</sub> '                           | (780+1344)  |                                  |                              |
| 31367 m                        | 2217                         | e' + a <sub>1</sub> '                           | (780+1449)  |                                  |                              |
|                                |                              | 2 × a <sub>1</sub> '                            | (1148)      | 31456 w                          | 2305                         |
|                                |                              | 2 × a <sub>1</sub> '                            | (1399)      | 31822 w                          | 2671                         |
| 31888                          | 2738                         | e' + a <sub>1</sub> '                           | (1293+1449) |                                  |                              |
|                                |                              | 2 × a <sub>1</sub> '                            | (1379)      | 31898 w                          | 2747                         |
| 31969                          | 2819                         |   |             |                                  |                              |

<sup>†</sup> The symmetry assignment has been made in comparison with the fundamental frequencies in the IR and Raman spectra.<sup>15</sup>

Table 2. Analysis<sup>†</sup> of the two-photon excitation spectrum of the  $S_2 \leftarrow S_0$  transition.

| two-photon<br>excitation of $S_2$ |                             | possible assign-<br>ment and ground<br>state vibrations |      |
|-----------------------------------|-----------------------------|---|------|
| $2 \times h\nu \text{ cm}^{-1}$   | $\Delta\nu \text{ cm}^{-1}$ |   |      |
| 32043 w                           |                             |   | 0,0  |
| 32668 s                           | 625                         | e'  | 619  |
| 32770 s                           | 727                         | e''   | 711  |
| 32840 s                           | 797                         | e'  | 780  |
| 32857                             | 814                         |   |      |
| 32928 m                           | 885                         | e''   | 868  |
| 32966 m                           | 923                         | e''   | 936  |
| 33096 w                           | 1053                        | e'  | 1052 |
| 33204 w                           | 1161                        | e'  | 1162 |
| 33295 w                           | 1291                        | e'  | 1300 |
| 33400 w                           | 1357                        |   |      |
| 33444 w                           | 1401                        | e'  | 1434 |

<sup>†</sup> The symmetry assignment has been made by comparison with the ground state frequencies.<sup>15</sup>

#### FIGURE CAPTIONS

Figure 1. A comparison (on the same energy scale) of the one- (A) and two- (B) photon excitation spectra of triphenylene in n-heptane single crystals at 1.6 K in the  $S_1 \leftarrow S_0$  absorption region.

Figure 2. The one- (A) and two- (B) photon excitation spectra of triphenylene in n-heptane single crystals at 1.6 K in the  $S_2 \leftarrow S_0$  absorption region.

